

Non-equilibrium Thermodynamics: Structural Relaxation, Fictive temperature and Tool-Narayanaswamy phenomenology in Glasses

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Abstract

Starting from the second law of thermodynamics applied to an isolated system consisting of the system surrounded by an extremely large medium, we formulate a general non-equilibrium thermodynamic description of the system when it is out of equilibrium. We then apply it to study the structural relaxation in glasses and establish the phenomenology behind the concept of the fictive temperature and of the empirical Tool-Narayanaswamy equation on firmer theoretical foundation.

I. INTRODUCTION

It is well known that when a liquid is disturbed suddenly from its equilibrium state by changing the temperature or pressure of the surrounding medium, or both, then the liquid undergoes a rapid, solidlike change, followed by a slower, liquidlike change towards the new equilibrium state. These changes can be seen in the variation in its thermodynamic properties such as the volume V or its enthalpy H with time. For a supercooled liquid, the above scenario plays an important role. As the temperature is lowered or the pressure is increased, the scale separation between the fast and the slow processes in supercooled liquids increases until the latter becomes too large compared to the experimental observation time τ_{obs} . In this case, the system is said to be kinetically arrested in that the liquidlike changes no longer contribute to the observed properties. The system behaves like a solid and is called a *glass* [1, 2, 3, 4, 5, 6].

The glass is a system that may be far from equilibrium so one cannot apply equilibrium statistical mechanics to investigate its properties, which vary with time. One must resort to apply non-equilibrium thermodynamics [7, 8], not a well-established field at present, to study glasses and their relaxation in time; the latter are usually known as *structural relaxation*. It is known from the early work of Littleton [9], and Lillie [10] that the isothermal viscosity of a glass changes during relaxation, thus implying the dependence of the relaxation on changes in the state of the glass [11]. The most general framework for developing non-equilibrium thermodynamics must satisfy the second law of thermodynamics or must start from it. The generality arises since the second law is independent of the processes (structural or otherwise) going inside the system. It is also independent of the details of the system considered and does not require any sophisticated concepts like ergodicity or its loss, etc. Our main goal in this work is to develop an appropriate non-equilibrium thermodynamics, which will then be applied to glasses with the hope to gain some new insight and to clarify at the fundamental level certain concepts extensively used in glasses.

Glassy behavior and their properties have been extensively studied and usually explained by invoking empirical rules [6, 12, 13] that, although they have proved invaluable and very reliable, lack theoretical justifications [3, 4]. Only recently, attempts have been made [14, 15] that use modern framework to investigate non-equilibrium properties of glassy relaxation at the molecular level. Our treatment here differs from these attempts in that we develop our

approach using the second law that should be applicable to all systems including glasses. We do not derive the actual laws of relaxation for which one must turn to other sources such as [14, 15]. Our goal is quite different. We wish to understand some of the important concepts used for glasses at a fundamental level. One of the most widely used concept in this field is that of the *fictive temperature*, first introduced by Tool [12] in an empirical fashion to describe non-linear relaxation in glasses. The system under study slows down so much upon reducing the temperature from its initial value T' , where the system was in equilibrium, to some temperature T_0 that one has to wait for a very long time before true equilibrium is reached at the final temperature. In this case, crudely speaking, the glass properties are assumed to be similar to a fictive liquid at some intermediate temperature between T' and T_0 . As time goes on and as the system undergoes structural rearrangements to come to equilibrium, the temperature of the system continues to change and finally becomes T_0 . This already means that the fictive temperature of the system continuously changes from T' to T_0 . Despite its continual usage in the field, the true meaning of the fictive temperature, though phenomenologically obvious, is not well-defined in terms of fundamental quantities such as the entropy. In particular, there exists a variety of fictive temperatures, each associated with the relaxing quantity under investigation, which makes the concept not very rich.

There is another aspect of structural relaxation. Its presence means that the glass is a non-equilibrium state. Thus, its temperature must be changing during the process of relaxation. How does one define the *instantaneous temperature* of the liquid? The instantaneous temperature itself must relax to T_0 as time goes on. Thus, there will a relaxation time describing the relaxation of the temperature of the glass. Tool [12] and Narayanaswamy [13], among others, observed that the relaxation time not only depends upon the temperature T_0 , but also depends upon the fictive temperature of the system; see for example [2, 3, 4]. Is the instantaneous temperature of the glass the same as the fictive temperature? These are important issues as a deeper understanding of these concepts will provide a more qualitative and predictive understanding of glass transition.

The layout of the paper is as follows. We consider an isolated system consisting of the system of interest surrounded by a very large medium and follow the consequences of it in the next section. In Sect. III, we follow the consequence of partial equilibrium to develop a very general non-equilibrium thermodynamics, which is then applied to a glass in Sect. IV. The concept of the fictive temperature and the Tool-Narayanaswamy phenomenology

are considered in Sect. V, and established on a firm theoretical ground. The conclusions are given in the last section.

II. CONSEQUENCES OF THE SECOND LAW

As said above, we study non-equilibrium systems by proceeding in a general manner by following the consequences of the second law, which is well established. As usual, we apply the second law to an isolated system, which we denote by Σ_0 ; it consists of the system Σ of interest (such as our glass) in a medium denoted by $\tilde{\Sigma}$ containing it. We will consider a single component system, which is sufficient for our purpose. According to the second law, the entropy S_0 of an isolated system Σ_0 can never decrease in time [16]:

$$\frac{dS_0(t)}{dt} \geq 0. \quad (1)$$

What happens inside the isolated system (loss of ergodicity in parts of the system, chemical reactions, phase changes, etc.) cannot affect the direction of the inequality, which makes it the most general principle of non-equilibrium thermodynamics. The law itself imposes no restriction on the actual rate of entropy change. In general, S_0 also depends on the number of particles N_0 , energy E_0 , and volume V_0 of Σ_0 . Thus, $S_0(t)$ used above should be really written as $S_0(E_0, V_0, N_0, t)$. However, as the extensive quantities remain constant in time there is no harm in using the compact form $S_0(t)$ during approach to equilibrium. The entropy $S_0(t)$ is a *continuous* function of each of its arguments. The energy, volume and the number of particles of Σ are denoted by E , V , and N , respectively, while that of the medium $\tilde{\Sigma}$ by \tilde{E} , \tilde{V} , and \tilde{N} . Obviously,

$$E_0 = E + \tilde{E}, \quad V_0 = V + \tilde{V}, \quad N_0 = N + \tilde{N}.$$

We will assume that N of the system is also fixed, which means that \tilde{N} is also fixed. However, the energy and volume of the system may change with t .

When the isolated system is in equilibrium, its entropy $S_0(E_0, V_0, N_0, t)$ has reached its maximum and no longer has any *explicit* time-dependence so that it can be simply written as $S_0(E_0, V_0, N_0)$ or S_0 . In this case, different parts of Σ_0 have the same temperature T_0 and pressure P_0 :

$$\frac{1}{T_0} = \frac{\partial S_0}{\partial E_0}, \quad \frac{P_0}{T_0} = \frac{\partial S_0}{\partial V_0}; \quad (2)$$

we have defined the temperature by setting the Boltzmann constant $k_B = 1$ in this work. Otherwise, the entropy $S_0(t)$ *continuously increases* and the isolated system is said to be not in equilibrium. The medium is considered to be very large compared to Σ , so that its temperature, pressure, etc. are not affected by the system. We assume $\tilde{\Sigma}$ to be in internal equilibrium (its different parts have the same temperature and pressure, but $\tilde{\Sigma}$ and Σ may not be in equilibrium with each other). Thus, its entropy \tilde{S} no longer has an explicit time dependence, but has an *implicit* t -dependence through the t -dependence of \tilde{E} , and \tilde{V} . The time variation of $S_0(t)$ is due to the relaxation going on inside Σ as it is driven towards equilibrium with the medium.

The entropy $S_0(t)$ of the isolated system can be written as the sum of the entropies $S(t)$ of the system and $\tilde{S}(t)$ of the medium:

$$S_0(E_0, V_0, N_0, t) = S(E, V, N, t) + \tilde{S}(\tilde{E}, \tilde{V}, \tilde{N}); \quad (3)$$

there is no explicit t -dependence in $\tilde{S}(\tilde{E}, \tilde{V}, \tilde{N})$ due to internal equilibrium. The correction to this entropy due to the weak stochastic interactions between the system and the medium has been neglected, which is a common practice [16]. We expand S_0 in terms of the small quantities of the system [16]

$$\tilde{S}(\tilde{E}, \tilde{V}, \tilde{N}) \simeq \tilde{S}(E_0, V_0, \tilde{N}) - \left(\frac{\partial \tilde{S}}{\partial \tilde{E}} \right) \bigg|_{E_0} E(t) - \left(\frac{\partial \tilde{S}}{\partial \tilde{V}} \right) \bigg|_{V_0} V(t).$$

It follows from the internal equilibrium of $\tilde{\Sigma}$ that

$$\left(\frac{\partial \tilde{S}}{\partial \tilde{E}} \right) \bigg|_{E_0} = \frac{1}{T_0}, \quad \left(\frac{\partial \tilde{S}}{\partial \tilde{V}} \right) \bigg|_{V_0} = \frac{P_0}{T_0},$$

and $\tilde{S} \equiv \tilde{S}(E_0, V_0, \tilde{N})$, which is a constant, is independent of the system. Thus,

$$S_0(t) - \tilde{S} \simeq S(E, V, N, t) - E(t)/T_0 - P_0 V(t)/T_0. \quad (4)$$

Let us introduce

$$G(t) \equiv H(t) - T_0 S(t), \quad H(t) \equiv E(t) + P_0 V(t), \quad (5)$$

the time-dependent Gibbs free energy and enthalpy of the system Σ with the medium $\tilde{\Sigma}$ at fixed T_0 and P_0 . We thus finally have

$$S_0(t) - \tilde{S} = S(t) - H(t)/T_0 = -G(t)/T_0, \quad (6)$$

so that the behavior (1) of $S_0(t)$ of the isolated system leads to an very important conclusion about the Gibbs free energy of the system:

$$\frac{dG(t)}{dt} \leq 0. \quad (7)$$

The Gibbs free energy $G(t)$ decreases as the system relaxes towards equilibrium, a result quite well known. If we abruptly cool the system from some previous temperature such as T_g to a lower temperature, the Gibbs free energy at the new temperature remains equal to its value at the previous temperature at time $t = 0$. As it relaxes, $G(t)$ continuously decreases. It cannot increase without violating the second law.

We have given the essential steps in its derivation here not only for the sake of continuity as some of the intermediate steps will be needed later on, but also to make some important points, which we now list.

1. In deriving the above equation (6), no assumption about the system Σ has been made. In particular, we have not assumed any particular aspect of its non-equilibrium nature, such as a particular form of relaxation (Arrhenius or otherwise), loss of ergodicity, etc.
2. The identification of $S_0(t) - \tilde{S}$ with the Gibbs free energy $G(t)$ of Σ is generally valid under the assumption of the medium being large compared to Σ , which can be satisfied as well as we wish.
3. The Gibbs free energy $G(t)$ and the enthalpy $H(t)$ are determined by the temperature T_0 and the pressure P_0 of the large medium.
4. The continuity of $S_0(t)$ with respect to all of its arguments that was mentioned earlier also applies to the Gibbs free energy of the system.
5. The decrease in $G(t)$ must not be violated even when there is a loss of ergodicity in the system, as is commonly believed to occur in a glass transition.
6. For glasses, we have an additional experimental fact. The enthalpy remains continuous across the glass transition. The continuity of the enthalpy then implies that the entropy $S(t)$ also will remain continuous with respect to all of its arguments, as the system relaxes. This allows us to differentiate the entropy, which will be required in Sect. III.

III. NON-EQUILIBRIUM THERMODYNAMICS

When the equality in (1) occurs, different parts of Σ_0 (such as Σ and $\tilde{\Sigma}$) have the same temperature T_0 and pressure P_0 . Otherwise, they have different temperatures and pressures, in which case a common assumption made by almost all workers is that of partial equilibrium (see, for example, Landau and Lifshitz [16, see p. 13]) when Σ_0 is out of equilibrium; each part is in *internal equilibrium* (local equilibrium), which then allows us to define the temperature, pressure, etc. for each part, which may all be different. In this situation, their entropies have the maximum possible values for their respective energies and volumes, and the number of particles. As a result, they have no explicit t -dependence [see the equilibrium condition (2) above for Σ_0]; their variation in time comes from the time variation of their energies, volumes, etc. The entropy S of the system determines its instantaneous temperature $T(t)$ and pressure $P(t)$:

$$\frac{\partial S}{\partial E} = \frac{1}{T(t)}, \quad \frac{\partial S}{\partial V} = \frac{P(t)}{T(t)}. \quad (8)$$

These are standard relations for the entropy [16], except that all quantities except S in the above equations may have an *explicit* dependence on time t that will make S depend *implicitly* on time. Accordingly,

$$\frac{\partial S}{\partial t} = 0 \quad (9)$$

under internal equilibrium. Relations like (8) along with (9) for internal equilibrium are used commonly in non-equilibrium thermodynamics. For example, we use them to establish that heat flows from a hot body to a cold body; see for example Sect. 9 in Landau and Lifshitz [16]. The glassy state, in which the fast dynamics has equilibrated and the slow dynamics is extremely slow, will thus be treated as a state in internal equilibrium, although it is not in equilibrium (with the medium). This observation will be very important when we discuss the concept of the fictive temperature in Sect. V.

Recognizing that $S(t)$ has no explicit t -dependence, see (2), but is a function of $E(t)$ and $V(t)$ (N is kept a constant), we have for the differential $dS(t)$

$$dS(t) = \frac{1}{T(t)}dE(t) + \frac{P(t)}{T(t)}dV(t),$$

where we have used (8) and have allowed the pressure and the temperature of the system to be different from those of the medium for the sake of generality. The first law of

thermodynamics follows from this equation:

$$dE(t) = T(t)dS(t) - P(t)dV(t), \quad (10)$$

which does not depend on the temperature and pressure of the medium. In this form, the first law has the standard look with the first term representing the heat

$$dQ = T(t)dS(t) \quad (11)$$

added to the system and the second term without the sign denoting the work

$$dW = P(t)dV(t)$$

done by the system.

Using $H(t) = E(t) + P_0V(t)$ in (5), we find that

$$dH(t) = T(t)dS(t) + V(t)dP_0 + [P_0 - P(t)]dV(t), \quad (12)$$

where the last term appears due to the lack of equilibrium with the medium. Accordingly, the heat dQ , see (11), is no longer equal to $dH(t)$ at constant pressure P_0 of the medium:

$$dQ(t) = dH(t)|_{P_0} + [P(t) - P_0]dV(t).$$

The specific heat C_P at constant pressure is given by

$$C_P(t) \equiv \left(\frac{\partial H(t)}{\partial T_0} \right)_{P_0} + [P(t) - P_0] \left(\frac{\partial V(t)}{\partial T_0} \right)_{P_0}$$

However, obtaining the entropy of the system from the measured values of the specific heat requires care:

$$dS(t) = \frac{C_P}{T(t)}dT_0 \leq \frac{C_P}{T_0}dT_0,$$

which follows from (19), derived later.

The differential of $G(t)$, see (5), turns out to be

$$dG(t) = -S(t)dT_0 + V(t)dP_0 + [T(t) - T_0]dS(t) + [P_0 - P(t)]dV(t), \quad (13)$$

Again, the last two terms are corrections to $dG(t)$ due to the non-equilibrium nature of the system. We observe from (13) that

$$\begin{aligned} \left(\frac{\partial G}{\partial T_0} \right)_{P_0} &= -S(t) + [T(t) - T_0] \left(\frac{\partial S(t)}{\partial T_0} \right)_{P_0} - [P(t) - P_0] \left(\frac{\partial V(t)}{\partial T_0} \right)_{P_0}, \\ \left(\frac{\partial G}{\partial P_0} \right)_{T_0} &= V(t) + [T(t) - T_0] \left(\frac{\partial S(t)}{\partial P_0} \right)_{T_0} - [P(t) - P_0] \left(\frac{\partial V(t)}{\partial P_0} \right)_{T_0}. \end{aligned}$$

Again, the last two terms in each equation are the correction due to non-equilibrium nature of the process, and would be absent in an equilibrium process.

One can compare the Gibbs free energy differential in (13) with the approach developed by de Donder [17] and Prigogine [18]. The last two terms in (13) denote the contributions from two different structural order parameter or the degree of advancement. In the present context, the two parameters are determined by the instantaneous entropy and volume

$$\xi_1 \equiv \frac{S(t) - S(\infty)}{S(0) - S(\infty)}, \quad \xi_2 \equiv \frac{V(t) - V(\infty)}{V(0) - V(\infty)},$$

and the corresponding affinities are given by

$$A_1 \equiv -[T(t) - T_0][S(0) - S(\infty)], \quad A_2 \equiv [P(t) - P_0][V(0) - V(\infty)].$$

Thus, we have

$$[T(t) - T_0]dS(t) - [P(t) - P_0]dV(t) \equiv -A_1\xi_1 - A_2\xi_2,$$

so that each contribution $A_i\xi_i \leq 0$, as expected from the variation of $G(t)$ during relaxation at constant T_0, P_0 . We also note that we can write the first law as

$$dE(t) = T_0dS(t) - P_0dV(t) - A_1\xi_1 - A_2\xi_2, \tag{14}$$

as expected from the standard formulation by de Donder.

IV. RELAXATION BELOW THE GLASS TRANSITION

We now apply the above formalism to a glass. Above the glass transition temperature T_g but below the melting temperature, the system is a supercooled liquid (SCL) as the relaxation time τ of Σ remains less than the observation time τ_{obs} . At T_g , they become identical. Below T_g , τ becomes larger than τ_{obs} , and the system turns into a glass. Let us consider the system in the glassy state. With time, the glass (Σ) will relax so as to come to equilibrium (the corresponding SCL state obtained by increasing τ_{obs} to the relaxation time at that temperature) with the medium if we wait longer than τ_{obs} . It should be noted again that, due to the internal equilibrium of the system, there is no explicit t -dependence in S on the right side of (3) or (4). Accordingly, the t -dependence in S, H , and G is implicit through $E(t)$, and $V(t)$. In the following, the glass is considered to be formed under *isobaric*

conditions so the pressure of the medium is kept fixed at P_0 as its temperature is step-wise varied. Accordingly, its instantaneous pressure $P(t)$ is always equal to P_0 of the medium

$$P(t) = P_0, \quad (15)$$

but its temperature will in general be different than T_0 and vary in time, as we will show below. The initial enthalpy $H(0)$ at T_0 is the enthalpy of the glass at temperature T' , and $H(\infty)$ the value of the SCL enthalpy after complete relaxation at temperature T_0 . It is experimentally found that the enthalpy decreases with time during an isothermal relaxation so that

$$H(t = 0) > H(t \rightarrow \infty). \quad (16)$$

This decrease is a general property of thermodynamics which follows from the specific heat being non-negative. We first consider the case when T' is the glass transition temperature, so that the system is in the SCL state at T' . As $T' > T_0$, the enthalpy $H(0)$ of SCL at T' must be higher than the enthalpy $H(t \rightarrow \infty)$ of SCL at T_0 . The same is also true of the volume in many cases, which relaxes to a smaller value in an isothermal relaxation. However, this property of the volume is not a thermodynamic requirement. Accordingly, as a general rule

$$\frac{dH(t)}{dt} < 0, \quad (17)$$

during isothermal structural relaxation in glasses. In the following, we will only use the above general property of the enthalpy, and not of the volume. Now, if T' is below the glass transition, then from the result just derived, we conclude that $H(0)$ is even larger than the SCL enthalpy at T' . This even strengthens the above inequality (16).

Let us now turn to the time derivative of the entropy S_0 , which is changing because the energy and volume of Σ are changing with time [16]. Thus,

$$\begin{aligned} \frac{dS_0(t)}{dt} &= \frac{dS}{dt} - \frac{1}{T_0} \frac{dE(t)}{dt} - \frac{P_0}{T_0} \frac{dV(t)}{dt} \\ &= \left(\frac{\partial S}{\partial E} - \frac{1}{T_0} \right) \frac{dE(t)}{dt} + \left(\frac{\partial S}{\partial V} - \frac{P_0}{T_0} \right) \frac{dV(t)}{dt} \geq 0, \end{aligned}$$

as the relaxation goes on in the system Σ . It is clear that

$$\frac{\partial S}{\partial E} \neq \frac{1}{T_0}, \quad \frac{\partial S}{\partial V} \neq \frac{P_0}{T_0},$$

if $dS_0/dt > 0$. Thus, as long as the relaxation is going on due to the absence of equilibrium, the two inequalities must hold true. Accordingly, the derivative $\partial S/\partial E$, which by definition

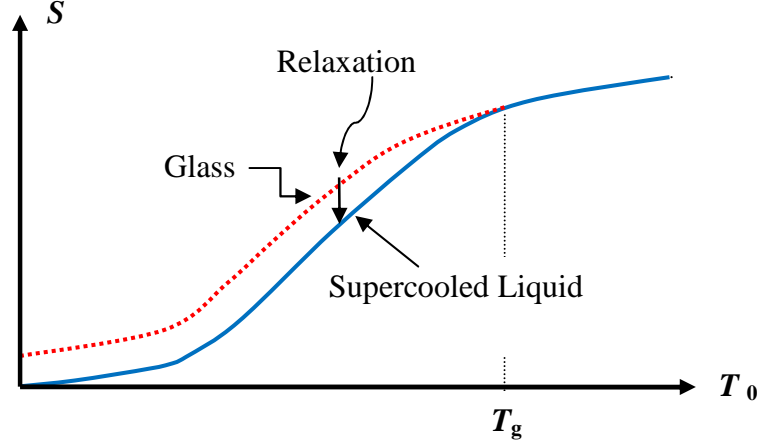


FIG. 1: Schematic behavior of the entropy for SCL (blue curve) and GL (red dotted curve). The GL entropy decreases, shown by the downward arrow, as it isothermally (constant temperature T_0 of the medium) relaxes towards SCL, during which its temperature $T(t)$ also decreases towards T_0 .

represents the inverse temperature $1/T(t)$ of the system, see (8), must be *different* from $1/T_0$ of the medium:

$$T(t) \neq T_0.$$

As $\partial S/\partial V = P_0/T(t)$, we see immediately that

$$\frac{dS_0(t)}{dt} = \left(\frac{1}{T(t)} - \frac{1}{T_0} \right) \frac{dH(t)}{dt} \geq 0. \quad (18)$$

From (17), we observe $dH(t)/dt < 0$ during relaxation in glasses. Thus, we are forced to conclude that

$$T(t) \geq T_0, \quad (19)$$

the equality occurring only when equilibrium has been achieved. The instantaneous temperature can be measured by using a small "thermometer" so as not to disturb the internal equilibrium of the glass. Such a measurement will allow us to explore its variation in time.

The above calculation also shows that

$$\frac{dS(t)}{dt} = \frac{1}{T(t)} \frac{dH(t)}{dt}, \quad (20)$$

which is the first term in (18). The equation above can also be obtained from (12). Using $P(t) = P_0$ for an isobaric process, which is the normal situation in most experiments, we see

that the last term in (12) vanishes. Hence,

$$dQ = dH(t) = T(t)dS(t)$$

is valid in all isobaric processes, from which (20) follows immediately.

The relaxation that occurs in the glass originates from its tendency to come to thermal equilibrium during which its temperature $T(t)$ varies with time; recall that we are considering a cooling experiment. The relaxation process results in the lowering of the corresponding Gibbs free energy, as is seen from (7), which is a consequence of the second law in (1). Accordingly, there are changes in its enthalpy and entropy, which are in the same direction; see (20). The lowering of $G(t)$ with time results in not only lowering the enthalpy in a cooling experiment, as observed experimentally, but also the entropy $S(t)$ during relaxation:

$$(dS(t)/dt) \leq 0,$$

as shown in Fig. 1. At constant P_0 and T_0 , we see from (13) that

$$dG(t) = [T(t) - T_0]dS(t), \tag{21}$$

from which it follows that

$$\frac{dG(t)}{dS(t)} = T(t) - T_0,$$

showing that $G(t)$ converges to its equilibrium value more slowly compared to the convergence of $S(t)$ as $T(t) \rightarrow T_0$, i.e. as $t \rightarrow \infty$ as the above derivative vanishes in this limit.

It is instructive to compare the specific heat of the glass with the specific heat of the corresponding fully relaxed state obtained as $t \rightarrow \infty$. Let us assume that at time $t = 0$, we change the temperature of Σ from some initial temperature T' to T_0 instantaneously. We consider the system at $t = t_{\text{obs}}$ and determine its enthalpy. The specific heat of the glassy sample at this instant is given by

$$C_{P,g} = \lim_{\Delta T \rightarrow 0} \frac{H(0) - H(t_{\text{obs}})}{\Delta T}.$$

Then, the corresponding specific heat after complete relaxation is given by

$$C_{P,\text{relax}} = \lim_{\Delta T \rightarrow 0} \frac{H(0) - H(\infty)}{\Delta T} \geq C_{P,g}.$$

V. THE FICTIVE TEMPERATURE AND THE TOOL-NARAYANASWAMY EQUATION

We now need to turn our attention to the distinction between the fast and slow degrees of freedom (dof), a characteristic of any glass. Situation similar to this also occurs in the attainment of thermal equilibrium between the nuclear spins and their environment during nuclear relaxation [19], where the spin-lattice relaxation is extremely slow. The explanation of this kind of behavior (slow and fast dof) in a wide class of substances lies in internal molecular motions other than simple vibrations. The fast dof cool down and equilibrate very fast, while the slow dof take much longer to transfer their energy and equilibrate because of very weak coupling with the surrounding medium. Here, we are talking about equilibration with the medium. We will denote those dof that have equilibrated with the medium at time t by a subscript "e", and the remaining that are not equilibrated by "n."

We set $t = 0$ at the instant the system is abruptly cooled from its equilibrium state at T' to some lower temperature T_0 of the medium. At this time, all dof are out of equilibrium with the medium at T_0 . The fast dof equilibrate within the observation time t_{obs} , with the slow dof remaining out of equilibrium [20]. Eventually, all dof come to equilibrium with the medium. Thus, the number of dof in equilibrium keeps on increasing with time. Let D denote the total number of the dof in the system, which is determined by the number of particles N in it; hence, it remains constant. Let $D_e(t)$ and $D_n(t)$ denote its partition in equilibrated and non-equilibrated dof, respectively:

$$D = D_e(t) + D_n(t);$$

evidently, they keep varying in time. As said above, the clear distinction between the two kinds of dof arises because of a very weak coupling between them and of the slow dof with the medium. The weak coupling allows us to treat them as almost uncorrelated and *quasi-independent*, which then immediately leads to the following partition of the entropy, the energy and the volume into two contributions, one from each kind because of their quasi-independence mentioned above:

$$S(t) = S_e(t) + S_n(t), \tag{22a}$$

$$E(t) = E_e(t) + E_n(t), \tag{22b}$$

$$V(t) = V_e(t) + V_n(t), \tag{22c}$$

where the notation is self-evident. It should be noted that $S_e(t)$ and $S_n(t)$ stand for $S_e(E_e(t), V_e(t))$ and $S_n(E_n(t), V_n(t))$. The corrections to each of the partition due to the very weak coupling is small enough to be neglected.

One should not confuse dof_e with only fast dof. To see this most clearly, we recall that at $t = 0$, none of the dof have equilibrated at the new temperature T_0 , so that $D_e(t = 0) = 0$. But all of the same dof were equilibrated at T' , implying that dof_e at T' contains fast and slow dof. The same happens as $t \rightarrow \infty$, in which case $D_e(t) \rightarrow D$ at T_0 implying that all dof, fast and slow, have equilibrated. Thus, in general, $D_e(t)$ contains both fast and slow dof. Let us now consider dof_n . At $t = 0$, none of the dof have equilibrated at the new temperature T_0 . Accordingly, $D_n(t = 0) = D$, so that dof_n contains both fast and slow dof. However, for $t > t_{\text{obs}}$, only (or mostly) the slow dof remain in $D_n(t)$.

Let us now introduce the following derivatives of the energy partitions

$$x(t) \equiv \frac{dE_e(t)}{dE(t)}, \quad 1 - x(t) \equiv \frac{dE_n(t)}{dE(t)}, \quad (23)$$

at a given t , so that

$$\frac{\partial S_e(t)}{\partial E(t)} = x(t) \frac{\partial S_e(t)}{\partial E_e(t)}, \quad \frac{\partial S_n(t)}{\partial E(t)} = [1 - x(t)] \frac{\partial S_n(t)}{\partial E_n(t)}. \quad (24)$$

The derivatives in the two equations above are at fixed $V_e(t)$ and $V_n(t)$, respectively. At $t = 0$, $D_e(t = 0) = 0$, $E_e(t = 0) = 0$ and $x(t = 0) = 0$. At $t \rightarrow \infty$, $D_e(t) \rightarrow D$, $E_n(t) = 0$ so that $x(t) = 1$. As time goes on, more and more of the "n" dof equilibrate, thus increasing $D_e(t)$ and $x(t)$.

By definition, we have

$$\frac{\partial S_e(t)}{\partial E_e(t)} = \frac{1}{T_0},$$

which follows from the equilibrium of the dof_e with the medium, while the dof_n will have a temperature different from this. Accordingly, we introduce a new temperature $T_n(t)$, defined by the derivative

$$\frac{\partial S_n(t)}{\partial E_n(t)} = \frac{1}{T_n(t)}. \quad (25)$$

The following identity

$$\frac{1}{T(t)} = \frac{x(t)}{T_0} + \frac{1 - x(t)}{T_n(t)} \quad (26)$$

easily follows from considering $\partial S(t)/\partial E(t)$ and using (22a) and (24). Initially, $x(0) = 0$ so that $T(0) = T_n(0) = T'$, while $T(t) \rightarrow T_0$ as $t \rightarrow \infty$, as expected. This division of

the instantaneous temperature $T(t)$ into T_0 and $T_n(t)$ is identical in form to that suggested by Narayanaswamy [13], except that we have given thermodynamic definitions of the non-linearity parameter $x(t)$ in (23) and of the new temperature $T_n(t)$ (25) in our approach. Both these quantities, being intensive, can only depend on energy and volume per particle, through which these quantities gain their implicit t -dependence.

Let us now understand the significance of the above analysis. The partition of the thermodynamic quantities in (22) along with the definition of the fraction $x(t)$ shows that the partition satisfies a lever rule: the relaxing glass can be *conceptually* (but not physically) thought of as a "mixture" consisting of two different "components" corresponding to dof_e and dof_n : the former is at temperature T_0 and has a weight $x(t)$; the latter with a complementary weight $1 - x(t)$ is at a temperature $T_n(t)$. Thinking of a system conceptually as a "mixture" of two "components" is quite common in theoretical physics. One common example is that of a superfluid, which can be thought of as a "mixture" of a normal viscous "component" and a superfluid "component" [21, Sect. 23]. In reality, there exist two simultaneous motions [21], one of which is "normal" and the other one is "superfluid". A similar division can also be carried out in a superconductor: the total current is a sum of a "normal: current and a "superconducting current" [21, Sect. 44].

The division of the dof envision above is no different from these divisions in a superfluid or a superconductor. However, because of the non-equilibrium nature of the system, there is an important difference here compared to a superfluid or a superconductor. The e-component is in equilibrium (with the medium), but the n-component is only in internal equilibrium. While the significance of the former as a SCL "component" at T_0, P_0 ($\text{dof}=D_e$) is obvious, the significance of the latter requires clarification. At $t = 0$, $T_n(t)$ represents the temperature T' of the equilibrated SCL ($\text{dof}=D$) from which the current glass is obtained by cooling. At this time, the entropy $S_n(t = 0)$ of initial state of the glass at T_0 is equal to the entropy $S_{\text{SCL}}(T')$ of the equilibrated SCL ($\text{dof}=D$) at the previous temperature T' . The latter has the energy and volume $E_{\text{SCL}}(T') = E_n(t = 0)$ and volume $V_{\text{SCL}}(T') = V_n(t = 0)$. At any later time $t > 0$, $T_n(t)$ represents the temperature associated with the energy $E_n(t)$ and volume $V_n(t)$ of the non-equilibrated "component" of the glass and has a weight $1 - x(t)$. This "component," being in internal equilibrium, can be identified as a *fictive* SCL [$\text{dof}=D_n(t)$] at temperature $T(t) < T'$ of energy $E_{\text{SCL}} = E_n(t)$ and volume $V_{\text{SCL}} = V_n(t)$. In other words, the relaxing glass at any time t can be considered as consisting of two SCL "components,"

one at temperature T_0 [dof= $D_e(t)$] and the other one [dof= $D_n(t)$] at temperature $T_n(t)$. The temperature $T \equiv T_n(t)$ *uniquely* determines the energy $E_{\text{SCL}}(T) \equiv E_n(t)$ and volume $V_{\text{SCL}}(T) \equiv V_n(t)$ of the corresponding *fictive* SCL [dof= $D_n(t)$].

As the fictive liquid at $T \equiv T_n(t)$ contains only (or mostly) the slow dof, it does not yet really represent a SCL associated with the system at $T \equiv T_n(t)$, as the former lacks dof_e, while the latter contains all dof. This does not pose any problem as the missing dof_e at $T \equiv T_n(t)$ are in equilibrium not only with the dof_n at $T \equiv T_n(t)$, the fictive SCL mentioned above, but also with the medium at $T \equiv T_n(t)$. Thus, one can consider "adding" these missing dof_e (dof= D_e) to the fictive liquid, which now represents the equilibrated SCL (dof= D) at $T \equiv T_n(t)$. This SCL is not the same as the glass with its fictive $T_n(t)$, as the latter has its dof_e at T_0 while the SCL has all of its dof at $T_n(t)$. However, all of their thermodynamic properties associated with dof_n must be the same, as their entropy function is the same for both liquids. Similarly, the SCL "component" at T_0, P_0 (dof= D_e) should also be "supplemented" by the missing dof_n to give rise to the equilibrated SCL at T_0, P_0 (dof= D).

We are now in a position to decide which of the temperatures $T(t)$ and $T_n(t)$ qualifies as the *fictive temperature*. This temperature is supposed to characterize the non-equilibrium aspect of the system. As $T(t)$ contains information about both kinds of dof, it is not the appropriate temperature to be identified as the fictive temperature, even though it depends on t . The temperature $T_n(t)$, on the other hand, depends only on non-equilibrated dof_n, and should be identified as the fictive temperature of the relaxing glass at time t . This temperature is not the internal temperature of the glass at this time, but represents the equilibrium temperature of the corresponding SCL at $T \equiv T_n(t)$ as noted above.

As first pointed out by Littleton [9] and Lillie [10], and discussed by several authors, see for example [4, 6, 11], the viscosity keeps changing with time during relaxation. Thus, if one uses an Arrhenius form for the viscosity, it must depend not on T_0 , but on $T(t)$; it is the instantaneous temperature that characterizes the instantaneous state of the glass. Thus, the Arrhenius form for the viscosity, which is usually taken to be proportional to the relaxation time, must be expressed as

$$\eta(t) = \eta_0 \exp \left[\frac{B}{T(t)} \right] = \eta_0 \exp \left[B \left(\frac{x(t)}{T_0} + \frac{1-x(t)}{T_n(t)} \right) \right], \quad (27)$$

the form conventionally identified as the phenomenological Tool-Narayanaswamy form.

Here, η_0 and B are some parameters of the system and may depend on T_0, P_0 and also weakly on time t . Our derivation above justifies this form on a solid theoretical ground.

One can carry out a similar analysis with decomposing the volume; see (22c). However, we do not obtain any new result as $P(t) = P_0$. To see this, we proceed exactly as above but use the volumes instead of the energies. Introducing the parameter $x_v(t)$ defined by

$$x_v(t) \equiv \frac{\partial V_e(t)}{\partial V(t)},$$

at fixed $E_e(t)$, which may be different from $x(t)$, and using

$$\frac{\partial S_e(t)}{\partial V_e(t)} = \frac{P_0}{T_0}, \quad \frac{\partial S_n(t)}{\partial V_n(t)} = \frac{P_0}{T_{n,v}(t)},$$

at fixed $E_e(t)$ and $E_n(t)$, respectively, along with $\partial S(t)/\partial V(t) = P_0/T(t)$, see (8) and (15), we find the following decomposition of the inverse instantaneous temperature

$$\frac{1}{T(t)} = \frac{x_v(t)}{T_0} + \frac{1 - x_v(t)}{T_{n,v}(t)}.$$

Now, the new fictive temperature $T_{n,v}(t)$ represents the temperature $T = T_{n,v}(t)$ of corresponding fictive SCL [dof= $D_n(t)$] with energy and volume $E_{\text{SCL}}(T) = E_n(t)$ and volume $V_{\text{SCL}}(T) = V_n(t)$. This fictive liquid is the same as noted above as far as the energy and volume are concerned. However, as SCL is an equilibrated state, the specification of energy and volume *uniquely* determines the temperature, which from the earlier analysis was seen to be exactly $T_n(t)$. Thus, we conclude

$$T_{n,v}(t) \equiv T_n(t).$$

In order for the above decomposition to be consistent with (26) at all times, we must ensure that

$$x_v(t) = x(t).$$

In other words, our definition of the fictive temperature gives the same value whether we consider the energy relaxation or the volume relaxation.

It is highly likely that the slow relaxation consists of many different relaxation modes, which we index by $j = 1, 2, \dots$. However, there does not seem to be any strong argument to suggest that all these different relaxation modes are almost decoupled as was the case for the fast and slow relaxations [20] studied above. In that case, it is not possible to partition the thermodynamic quantities such as the entropy, etc. associated with dof_n as a sum over

these different modes. Despite this, let us follow the consequences of such an assumption. We express $D_n(t)$ as a sum over j

$$D_n(t) \equiv \sum_j D_n^{(j)}(t),$$

where the notation is quite transparent. We similarly express all of the n -quantities in (22) as a sum over j . We can similarly express

$$1 - x(t) \equiv \sum_j y_j,$$

where

$$y_j \equiv \frac{dE_n^{(j)}(t)}{dE(t)}.$$

We can now introduce a fictive temperature for each j -th n -dof

$$\frac{\partial S_n^{(j)}(t)}{\partial E_n^{(j)}(t)} = \frac{1}{T_n^{(j)}(t)},$$

such that

$$\frac{1 - x(t)}{T_n(t)} \equiv \sum_j \frac{y_j}{T_n^{(j)}(t)},$$

a decomposition also described by Narayanaswamy [13]. However, because of the above equality, the presence of more than one kind of relaxation modes does not change the earlier decomposition (26). In other words, no new insight is gained by such an assumption. One can introduce an equilibrated fictive SCL at each of the fictive temperatures as above. We will not stop here to do so as it is straightforward.

VI. CONCLUSIONS

We have developed a non-equilibrium thermodynamics to study systems away from equilibrium. The approach is quite general and is not limited to systems close to equilibrium. Assuming internal equilibrium, a common practice in the field, we find the correction to the differential free energies that are consistent with de Donder-Prigogine approach to non-equilibrium thermodynamics; see for example (14). Even though, we have mainly discussed supercooled liquids, the approach does not require the presence of a melting transition and an equilibrium crystal for its application. Thus, it should also be applicable to other glassy

systems such as spin glasses, where there is no equilibrium crystal as the true equilibrium state. The only requirement is that enough time has passed after the system has been disturbed so that the instantaneous temperature, pressure, etc. can be defined via (8) for the system even if they are changing with time. In other words, there is partial equilibrium in the isolated system. We then apply this thermodynamics to study glasses and clarify the concept of the fictive temperature $T_n(t)$ widely used in the study of glasses by identifying it as a thermodynamic quantity; see (25). Our analysis shows that the fictive temperature has the same value even if we change the relaxing quantity. This temperature is not identical to but is related to the instantaneous temperature $T(t)$ in a glass; see (26). We use this relationship to establish the Tool-Narayanaswamy equation (27) for the relaxation time on a solid theoretical ground. This form does not change even if we have more than one kind of slow relaxation; the latter results in many different fictive temperatures, one for each kind of slow relaxation.

We should finally contrast our approach with other approaches available in the literature. We can use (22a) to express $dS(t) = dS_e(t) + dS_n(t)$. However, each term is still multiplied by $T(t)$, implying that $dS_e(t)$ or $dS_n(t)$ are not multiplied by their respective temperatures T or $T_n(t)$. Thus, one cannot consider $S_e(t)$ and $S_n(t)$ as separate in the first law (10) or in (21). This should be contrasted with the approach developed in [22], where the entropy is divided into fast and slow dof; see also [23]. More recently, Möller et al [24] have used the approach of de Donder to study glasses by considering a single structural order parameter; however, the concept of the fictive temperature was not analyzed. A recent approach by Wolynes [14, (b)] provides a local description of the relaxation in an inhomogeneous mosaic form, but the interest is in the dynamics, whereas our focus is not on any particular dynamics.

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